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Assessing the Feasibility of Measuring Carbonyls in Ambient Air with a Submillimeter Wave Spectroscopic Sensor

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Introduction

- Submillimeter wave (SMMW) spectroscopic gas sensor
  - Developed by Battelle and OSU for DARPA
  - Offers significant gains in sensitivity, selectivity, and speed
- Adaptable to air pollutant monitoring applications
  - Direct detection of formaldehyde, acrolein, NO_2, etc.
  - Simultaneous detection of multiple criteria pollutants
  - Reduced reliance on lab-based sample analysis

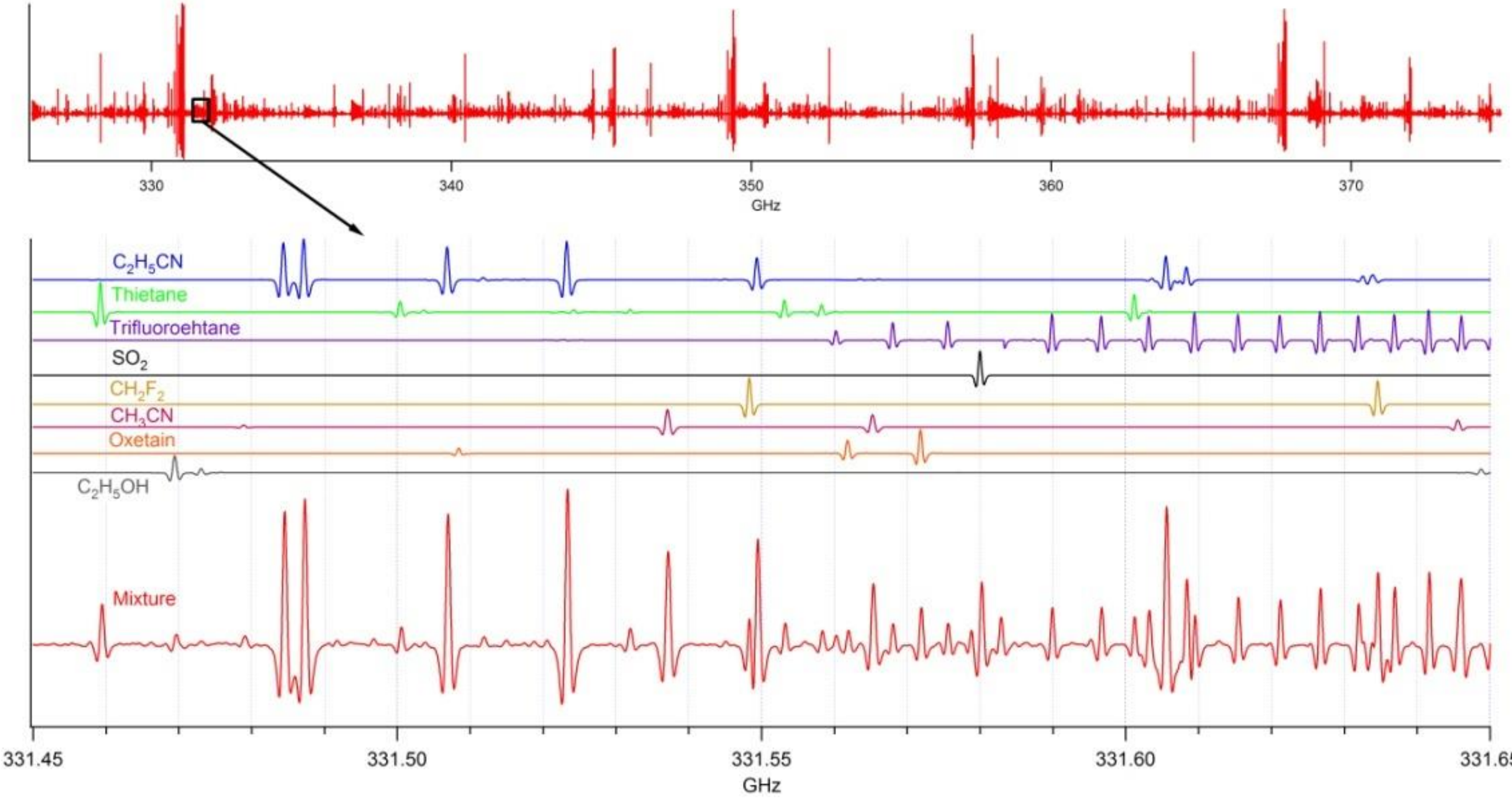
Overview

- Advantages of SMMW spectroscopy
- DARPA MACS sensor
- Relevance to gaseous pollutant detection
- EPA/OAQPS feasibility study
- Path forward, technology development roadmap

SMMW Spectroscopy

- High resolution SMMW spectroscopy exploits molecular rotational transitions
- Uniqueness and redundancy of signatures provide near-absolute specificity
  - Optimal pressure ~10 mTorr - Doppler limit
  - Small number of molecules required for detection
- Laboratory SMMW spectroscopy is very mature (50+ years)

Example Spectra



Advantages of SMMW Sensor

- Technology now available for small (1 ft^3) system (100-600 GHz)
- Potential for very high sensitivity (ppt) if incorporate preconcentration
- Very high specificity → Low false alarm rate
- Fast measurement and analysis (sec to min)
- Broad range of target analytes

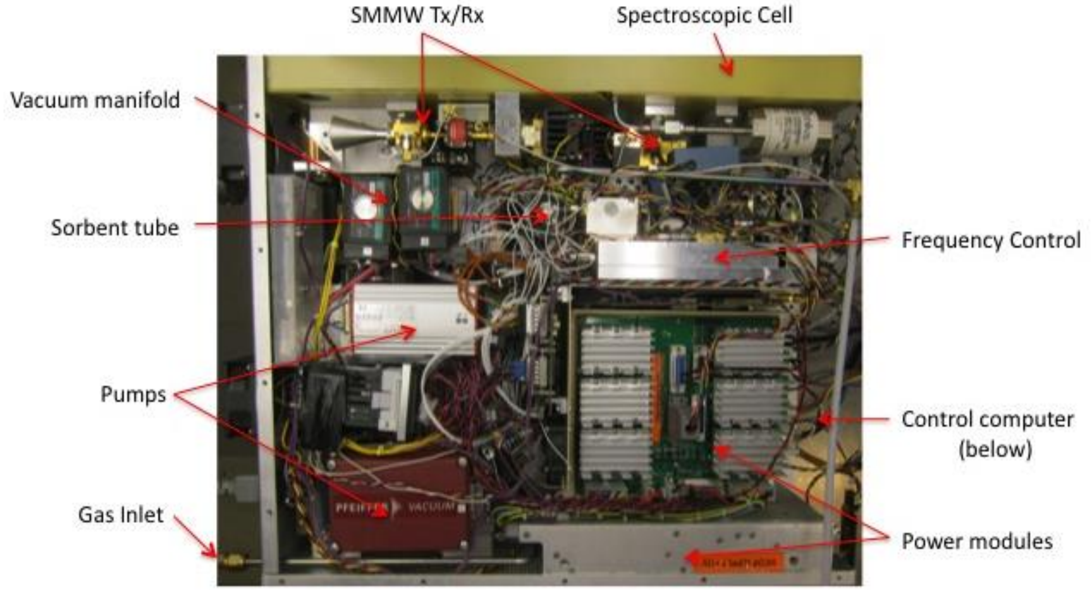
Neese, et al., "Compact Submillimeter/Terahertz Gas Sensor with Efficient Gas Collection, Preconcentration, and ppt Sensitivity," *IEEE Sensors Journal* vol. 12, pp. 2565-2574, 2012

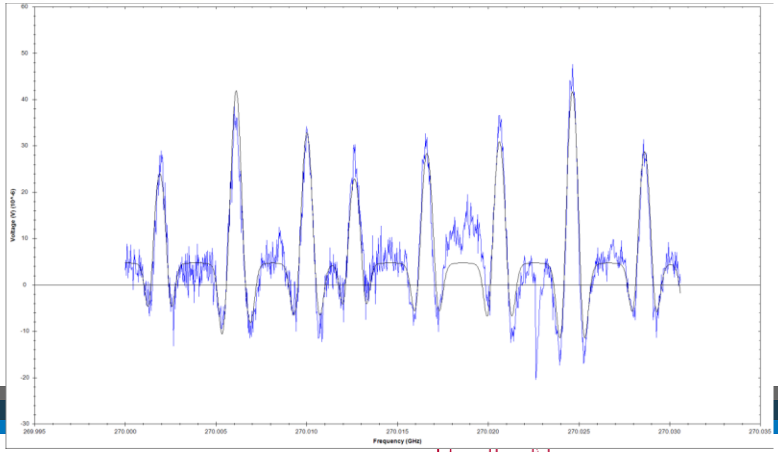
Disadvantages of SMMW Sensor

- System cost currently high for pollution monitoring applications (> $100k)
  - Continued tech development will drive down cost
- Dipole moment required
- Difficult to detect large/complex molecules
  - Additional research required to incorporate alternative techniques
- Some smaller molecules (NH_3, HF, etc.) require high frequency sources (600 GHz)

DARPA Mission Adaptable Chemical Sensor (MACS) Program

- Met or exceeded all DARPA metrics
  - Sensitivity: ~ppt
  - Selectivity: simultaneous detection of 30+ gases
  - False alarm rate: < 10^{-10}
  - Speed: 10 min
  - Size: 1 cubic foot



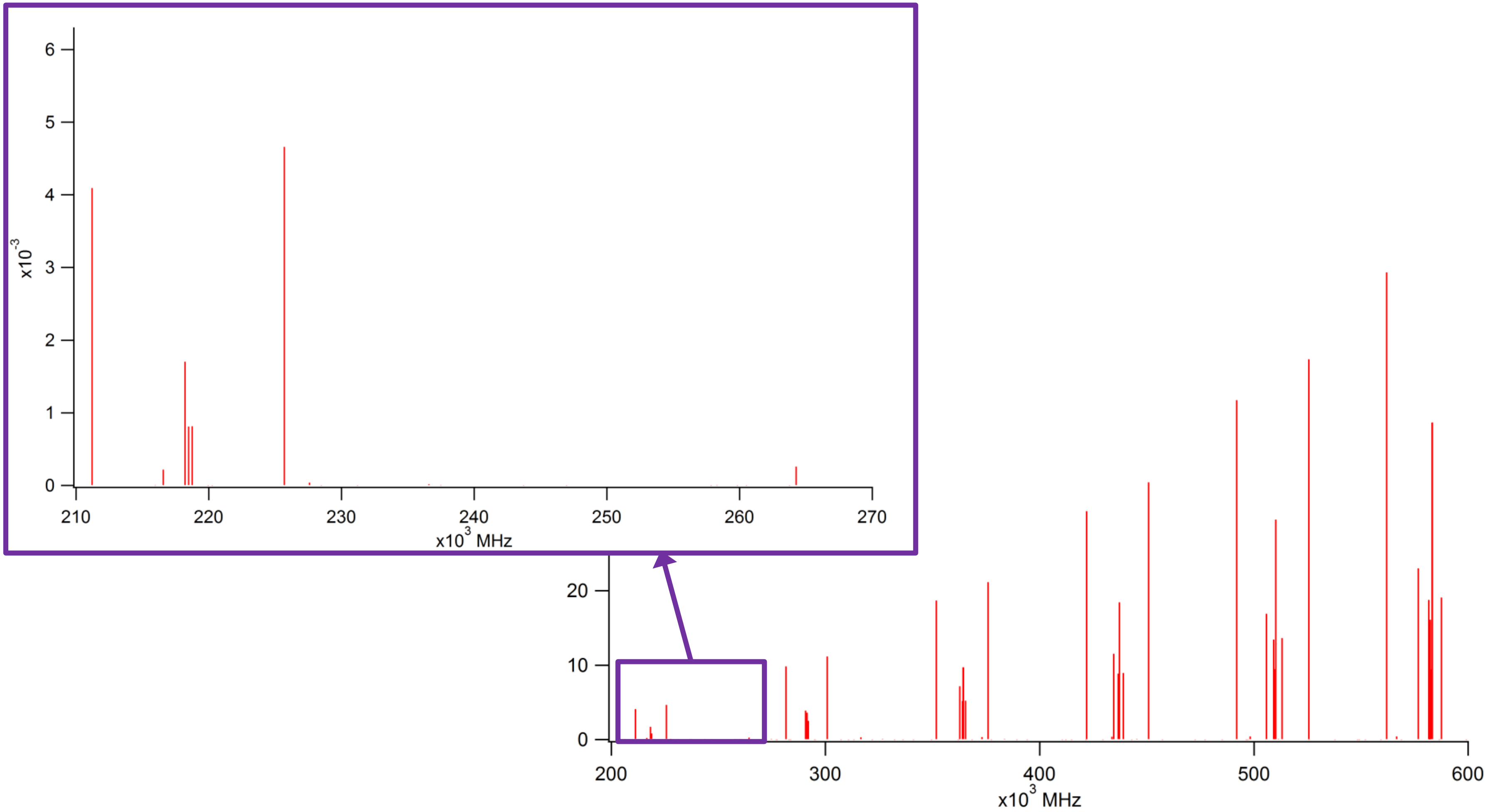


Detection of Gaseous Pollutants

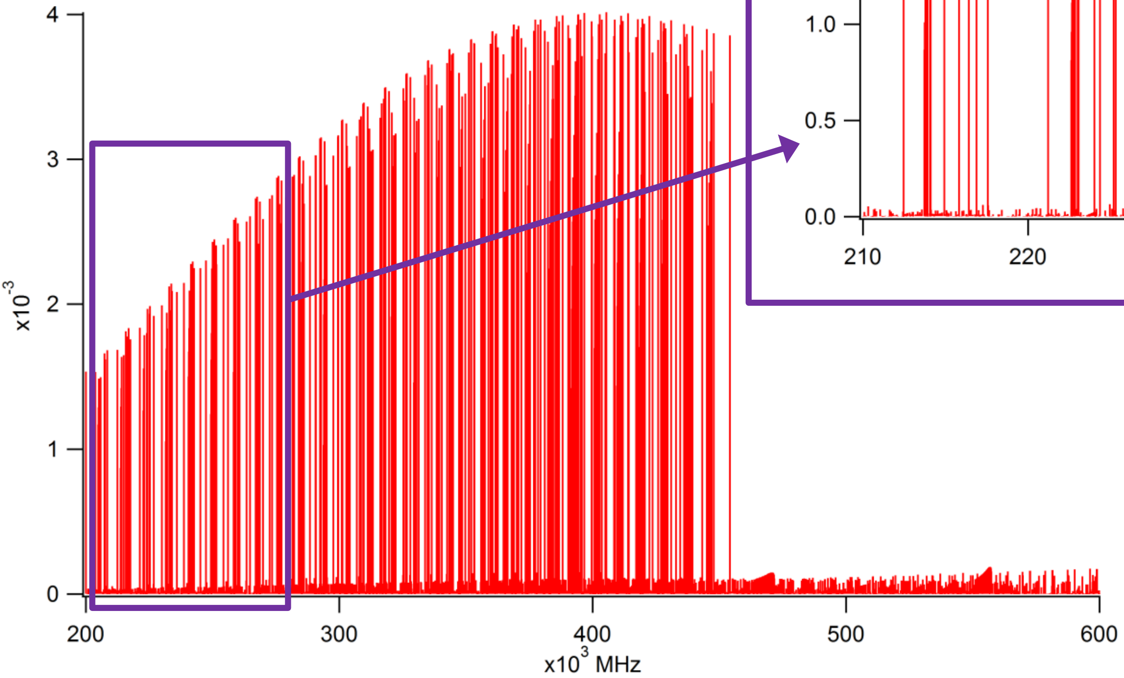
- Ability to detect carbonyls, NOx, SOx, etc.
- Simultaneous detection of multiple pollutants
- Sufficient sensitivity for air monitoring (ppb-ppt)
- Near real-time monitoring capability
- Maturation of technology expected to enable development of ~$20k system

Formaldehyde

Spectral data from NASA JPL catalog: http://spec.jpl.nasa.gov/



Acrolein



4
3
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1
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200
300
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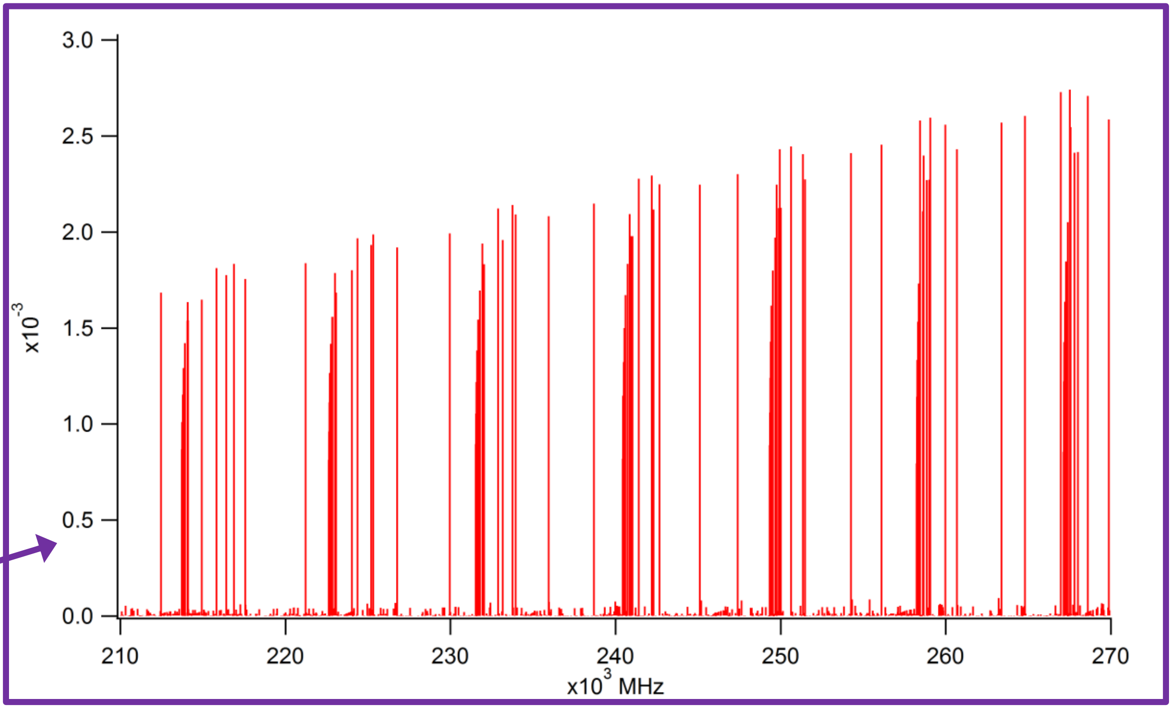

3.0
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x10-3
210
220
230
240
250
260
270
x10³ MHz

EPA/OAQPS Feasibility Study

- Objective
  - Investigation of SMMW detection limits for target air toxic compounds (formaldehyde, acrolein, acetaldehyde)
  - Investigation of preconcentration to enhance the sensitivity of the SMMW sensor for ambient air measurements

SMMW Detection Limits (OSU)

- Test planning
- Spectroscopic measurement of three carbonyls: formaldehyde, acrolein, and acetaldehyde
  - Standard spectrometer
  - Neat and diluted samples
- Estimation of method detection limit (MDL)
  - Assume no preconcentration
  - Correlate with relevant measurement parameters (resolution, detector sensitivity, cell conditions)

Preconcentration Study (Battelle)

- Literature search on preconcentration approaches for carbonyls
- Laboratory characterization of two approaches
  - Based on MACS sorbent characterization effort
  - Standard GC/MS methods
- Concentration efficiency estimation for each identified approach
- Estimation of overall SMMW MDL (spectra + preconcentration)

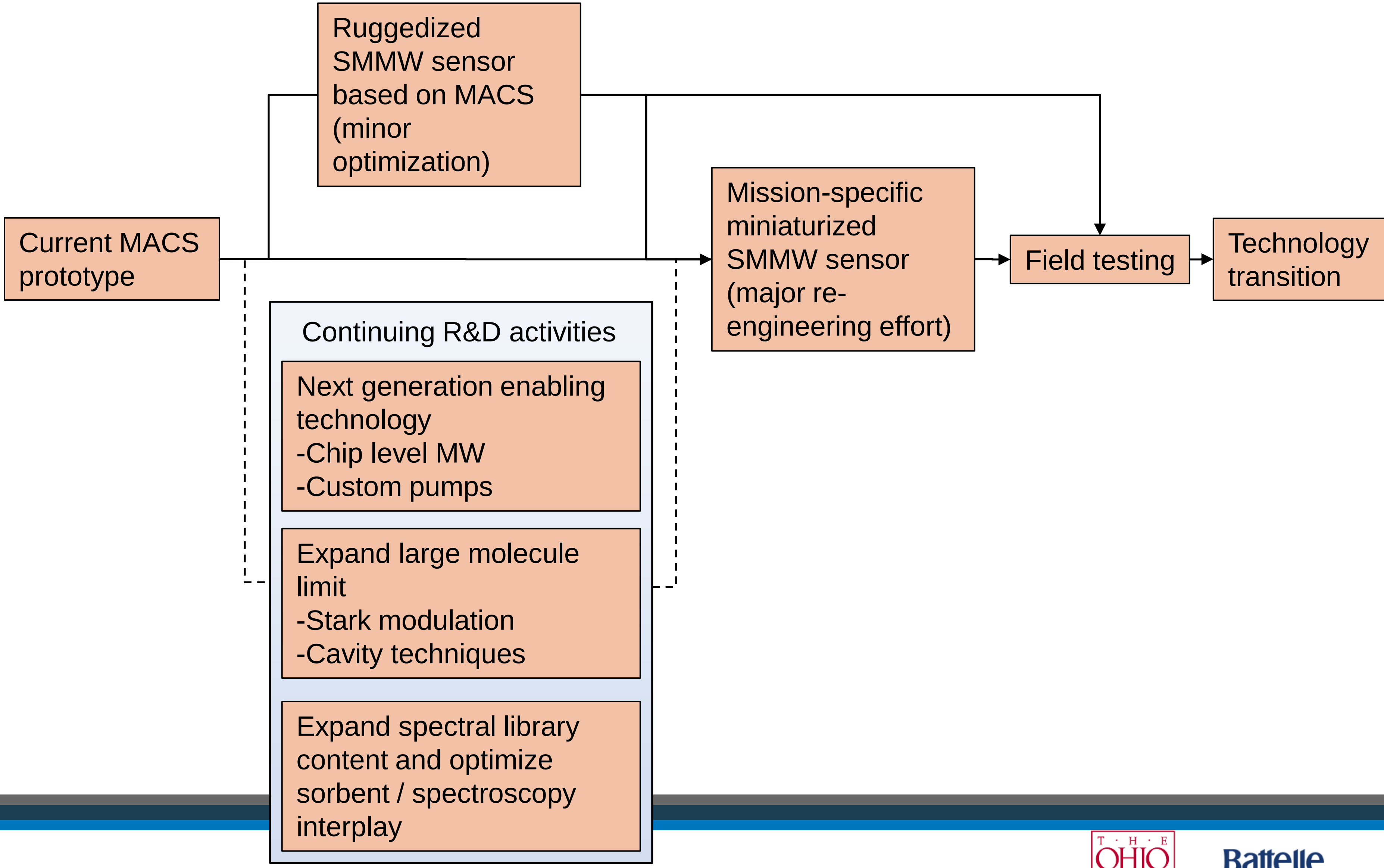
Status

- Test planning complete (draft QAPP)
- Theoretical calculations of SMMW sensitivity underway
- Literature search for preconc methods complete
  - Cryotrap
  - Semipermeable membranes
  - Carbon Nano Tubes (CNTs), functionalized and non-functionalized
  - Functionalized silicas
  - Sorbents (traditional, emerging, non-traditional)

Future Technology R&D

- Spectrometer cost reduction and miniaturization
  - Current MACS technology uses robust commercial MMW multipliers and amplifiers that cost ~$70K
  - Advances in wireless communications technology moving toward chip-level devices that can produce 100 GHz and cost ~$100
  - Leveraging advances in CMOS technology funded by Semiconductor Research Corp
  - Following advancements at IBM to extend current Tx/Rx of 60 GHz to ~240 GHz

Sensor Development Roadmap



Conclusion

- SMMW sensor provides flexibility to detect multiple air pollutants simultaneously in near real-time
- Concept proven by meeting performance metrics on DARPA MACS program
- Development of ruggedized, autonomous, inexpensive sensor is feasible
- Can broaden scope of air monitoring, fill gaps in continuous monitoring of formaldehyde and acrolein, offer direct NO_2 detection, and reduce lab-based sample analysis costs

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